Thermal Dimerization and Carbonylation of a Carbene in Low-temperature Matrices

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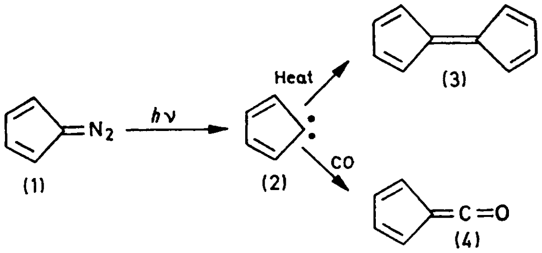
Summary The carbene, cyclopentadienylidene (**2**), produced by photolysis of diazocyclopentadiene (**1**) in low-temperature matrices, has been detected by i.r. and u.v. spectroscopy, and its thermal dimerization and reaction with carbon monoxide have been observed.

THE matrix-isolation technique[1] has recently met with some notable success in the identification of highly unstable organic molecules, for example cyclobutadiene.[2] We have studied the photolysis of matrix-isolated diazocyclopentadiene (**1**). Although photolysis of low-temperature glasses containing (**1**) gave rise to a product assumed, on the basis of its triplet e.s.r. spectrum,[3] to be the carbene (**2**), an earlier matrix u.v. study suggested that fulvalene (**3**) was the only identifiable product.[4] We report spectroscopic evidence (u.v. and i.r.) for the photochemical formation of the carbene, which undergoes subsequent thermal dimerization to give fulvalene. In the presence of carbon monoxide, the previously uncharacterized keten (**4**) is formed by thermal addition.[5]

In a nitrogen matrix, (**1**) had a strong broad u.v. absorption (λ_{max} 293 nm) and, in the i.r. spectrum of the same sample, a very strong ν(N=N) band (*ca.* 2100 cm^{-1}) and a series of much weaker bands (1600—400 cm^{-1}). When a very dilute matrix ($1 : 1{\cdot}5 \times 10^6$; 20 K) was irradiated with an unfiltered medium-pressure Hg arc, all the i.r. bands of (**1**) totally disappeared. The u.v. band of (**1**) was also observed to vanish, leaving a new broad band (λ_{max} 296 nm)



which was too intense by a factor of at least ten to be attributable to residual (**1**) (spectrum A). On repeating the experiment with a more concentrated matrix (1 : 1000; 20 K) spectrum B was obtained, showing the same broad absorption but with a series of intense sharp bands superimposed upon it. These sharp bands correspond to the published spectrum[4] of fulvalene. The i.r. spectra in both experiments showed several bands, the strongest being at 703 cm^{-1}, which were produced simultaneously with the broad u.v. band. All these bands were, apparently, due to a single compound, not fulvalene.

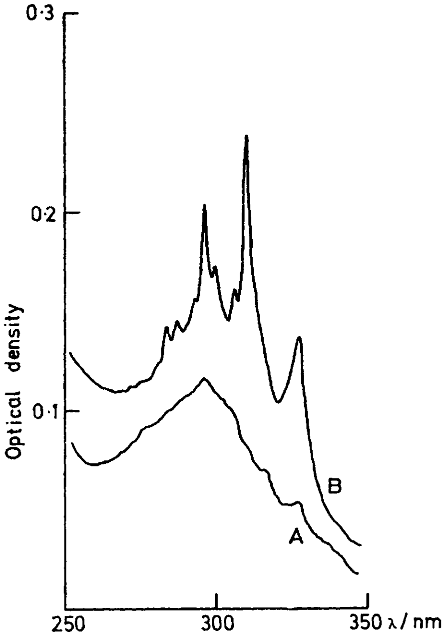


FIGURE. U.v. absorption spectra obtained after irradiation of (**1**) in nitrogen matrices. (A) 1 : 1·5 × 10^6 at 20 K; (B) 1 : 1000 at 20 K.

The amount of fulvalene formed during photolysis could be minimized by irradiation with filtered light ($\lambda > 300$ nm) at lower temperatures (12 K). Under these conditions, complete photolysis of (**1**) at 1 : 10,000 in a nitrogen matrix gave rise to a u.v. spectrum similar to spectrum A. Warming the matrix to 30 K and recooling to 12 K (annealing) resulted in a substantial increase in the intensity of the fulvalene u.v. bands and a small decrease in the intensity of the i.r. bands (703 cm^{-1} *etc.*). Thus fulvalene was formed thermally from an intermediate already present in the matrix. In a separate experiment at the same dilution, prolonged photolysis (30 min) of the intermediate caused the broad u.v. band and i.r. bands to disappear completely, leaving only a weak u.v. spectrum of fulvalene; the final products have so far remained undetected. Subsequent annealing of the matrix produced no increase in intensity of the fulvalene bands. Thus the broad u.v. absorption and associated i.r. bands can be assigned to the fulvalene precursor.

No i.r. bands attributable to fulvalene itself have been observed, presumably because they are weak compared to the intense u.v. spectrum. Previous identification of matrix-isolated fulvalene was based solely on u.v. spectra.[4]

When (**1**) was irradiated in a matrix of pure carbon monoxide (1 : 1000; 20 K), neither fulvalene nor the intermediate was observed. Instead, the appearance of i.r. bands at 2133, 2130 [ν(C=O), vs], 2082 and 2073 cm^{-1} [$\nu(^{13}C=O)$, vw] as well as bands at lower frequencies indicated the formation of a keten. Bands in the u.v. at 258 and 266 nm were also observed and a clean isosbestic point (λ 273 nm) could be obtained for the transformation of (**1**) into keten. The striking resemblance of the i.r. spectrum of the keten to that of (**1**) throughout the region 1600—400 cm^{-1} strongly supports the assignment of structure (**4**) to the keten.

In mixed matrices of nitrogen and carbon monoxide, (1 : 10,000; 12 K), the amounts of fulvalene and intermediate formed on initial photolysis decreased with increasing carbon monoxide concentration (1—20%). Subsequent annealing of these matrices resulted in further keten formation (growth of i.r. and u.v. bands) and a decrease in intensity of the bands of the intermediate without any corresponding increase in the fulvalene bands. Thus the same intermediate is involved in the thermal formation of both the keten and fulvalene.

On the basis of these experiments, we propose that the intermediate is the carbene (**2**), which undergoes the reactions illustrated.

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